BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

THE PREPARATION AND PROPERTIES OF

BARIUM TRITHIOCARBONATE

Submitted by

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Preface

Every student of inorganic chemistry has observed the similarity in the structural formulas of many compounds of oxygen and sulfur. The fact may have been pointed out to him by his instructor during the period in which he was attempting to master the vocabulary of the chemist, he may have become aware of it during his study of the periodic system, or it may have become gradually apparent to him. The structural similarity of such compounds as H_2O and H_2S, CO_2 and CS_2, and BaO and BaS, are well known. But the sulfur analogues of H_2CO_3 and its carbonate salts are not as well known. With the conviction that sulfur salts could be prepared bearing some resemblance to the well-known carbonate salts, the author commenced the investigation of trithiocarbonates which is recorded in this thesis.

In order to convince himself of the true nature of trithiocarbonates the author has not taken for granted, immediately, the work of previous investigators but has repeated much of their work and has attempted to add to our knowledge through research in the laboratory. To accomplish this most satisfactorily it has been necessary to restrict his personal investigation to the preparation and properties of barium trithiocarbonate.

The author wishes to thank Dr. Lyman C. Newell for his many suggestions, and for the interest he has shown in this thesis.

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Introduction

A Historical Resumé of the Results of Previous Investigators

The sulfur analogues of the metallic carbonates in which the positions of the three oxygen atoms of the carbonate radical are held by three sulfur atoms have become known as trithiocarbonates. The term thiocarbonates has been used by some investigators but, since the same term is used for the derivatives of mono-thiocarbonic acid, it will be avoided in this thesis. The author has made a study of the salt derivatives of trithiocarbonic acid, HS.CS.SH, which he has used as a foundation for his research on the preparation and properties of barium trithiocarbonate.

In 1826 Berzelius[1] published the results of his investigations on the reactions of carbon disulfide with soluble sulfides that had been noted by Zeise in 1824. Berzelius prepared soluble and insoluble trithiocarbonates of various metals by direct combination of carbon disulfide and the sulfides of the metals. He recognized the fact that the trithiocarbonates are unstable and give off carbon disulfide on decomposition. He attempted to analyze the crude trithiocarbonates which he prepared but met with defeat on every hand, and concluded that unstable trithiocarbonates could not be analyzed.

In 1844 Falieres[2] pointed out that large quantities of potassium trithiocarbonate, K_2CS_3, were being used in the

1. E. W. Yeoman, J. Chem. Soc. 119, 38-54 (1921)
2. Falieres, Ann. Chim. Phys. (6) 2, 134-144 (1844)

destruction of phylloxera, in place of free carbon disulfide which had been previously used. The K_2CS_3 was claimed to be preferable to free CS_2 which injured the vine. Falieres suggested a crude method of analysis in which the CS_2 was precipitated from the trithiocarbonate solution by adding H_2SO_3 and distilled into benzene. The increase in volume of the benzene was determined, and the industrial value of trithiocarbonate calculated. While this method of analysis gave the percentage of available CS_2 with sufficient accuracy for industrial purposes, it was found to be of little value to the author in his attempt to analyze barium trithiocarbonate.

In 1876 Mermet[3] published under the name of sulphocarbonates two articles concerning the qualitative nature of some metallic trithiocarbonates. He observed that the alkaline trithiocarbonates were all deliquescent and dissolved in water to form a reddish-colored solution. Mermet[4] suggested the following delicate test for trithiocarbonates: An alkaline solution of a nickel salt is diluted until almost colorless by adding NH_4OH and H_2O, and to this is added a few drops of the solution to be tested. A cherry-red tint is produced if over one part of trithiocarbonate per 60,000 parts of solution is present.

Fifty-seven years after the investigations of Berzelius, Sestini[5] presented a paper on the Preparation of Thiocarbonates for Destruction of Phylloxera. The suggested method was for the preparation of a mixture of K_2CS_3 and $CaCS_3$. Two hundred

3. Mermet, A., Bull. Soc. Chim. (2) XXIV, 433-434 (1876)
4. Mermet, A., Compt. rend., lxxxi, 344 (1876)
5. Sestini, Gazzetta Chim. Ital., 12, 476-82 (1883)

grams CS_2, 200 grams K_2CO_3, 200 grams CaO slaked with 100 grams H_2O, and 1000 grams H_2O, were refluxed at 60° C. for ten hours. During the same year (1883) Müntz[6] advanced a method of analysis of CS_2 in trithiocarbonates similar to that of Falieres. The essential differences in the methods are that $ZnSO_4$ was added to the trithiocarbonate solution in place of H_2SO_3, and that petroleum was used to collect the CS_2 in place of C_6H_6. Müntz claimed good analytical results.

In 1911 Tarngin and Magri[7] published the results of their investigation of K_2CS_3. They noted that a water solution of K_2CS_3 exposed to the sunlight would decompose in about two hours into K_2S and CS_2 with subsequent hydrolysis of the K_2S. They also noted that a similar solution in vacuo would not decompose as readily. The author of this thesis found that he was able to prevent the decomposition of trithiocarbonates by keeping them in a desiccator over CS_2. Tarngin and Magri also passed various gases through a water solution of K_2CS_3 while it was being heated to boiling. The following reactions are suggested as taking place:

N_2: $K_2CS_3 + 2H_2O \rightarrow CS_2 + 2KOH + H_2S$

Air: $2K_2CS_3 + 2H_2O + 2O_2 \rightarrow K_2S_2O_3 + K_2CO_3 + CS_2 + 2H_2S$

CO2: $K_2CS_3 + CO_2 + H_2O \rightarrow K_2CO_3 + CS_2 + H_2S$

By the year 1919 the interest in trithiocarbonates as a cure for Phylloxera seems to have abated and attention was being given to their removal from ammonia liquor in the gas

6. Muntz, A., Compt. Rend. 96, 1430-1433, (1883)
7. Tarngin, N. and Magri, A., Gazz. chim, ital., 39, I, 405-18 (1911)

grams CS_2, 200 grams K_2CO_3, 2-- grams CaO slaked with 100 grams H_2O, and 1000 grams H_2O, were refluxed at 50° C. for ten hours. During the same year (1883) Muntz[6] advanced a method of analysis of CS_2 in trithiocarbonates similar to that of Pollacci. The essential differences in the methods are that $CuSO_4$ was added to the trithiocarbonate solution in place of H_2SO_4, and that petroleum was used to collect the CS_2 in place of C_6H_6. Muntz claimed good analytical results.

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6. Muntz, A., Compt. Rend. 96, 1430-1433, (1883)
7. Tarugi, N. and Magri, A., Gazz. chim. ital., 41, I, 405-12 (1911)

works. The fifty-fifth annual report[8] (1918) on alkali works by the Chief Inspector (England) p. 53-74, suggests a method of getting an approximate measure of the amount of thiocarbonate in ammoniacal liquor. The percent of thiocarbonate is obtained by digesting the sample in absence of air, heating, if necessary, at 80°-90° C. The subsequent sulfide is removed by shaking with $PbCO_3$. The percent of thiocarbonates is calculated from the amount of PbS formed. Spielman and Wood[9] advised shaking with $ZnCO_3$ in addition to the $PbCO_3$ treatment. Linder, Colman, and Yeoman[10] at first emphasized the necessity of excluding air during the digestion, but later found that a conical flask with a loose stopper was sufficient, as the escaping vapors gave protection. Spielman and Wood[11] also suggested a coloration method for the determination of trithiocarbonates. This method was based on the comparison of the sample with standard solutions, but this method proved unsatisfactory due to colored impurities.

The most outstanding article concerning trithiocarbonates which appears in the literature is that by E. W. Yeoman* on Trithiocarbonates and Perthiocarbonates. Yeoman claims to have prepared in pure form and to have analyzed, by the usual empirical methods, the Na, K, NH_4, Ca, Sr, and Ba salts of H_2CS_3. Yeoman prepared pure hydrosulfides of the alkali metals by passing H_2S through alcoholic solutions of their ethoxides

8. Fifty-fifth Annual Report, J. Soc., Ch. Ind., 38, 716 A (1919)
9. Spielman and Wood, J. Soc. Ch. Ind., 38, 369-70 T (1919)
10. Linder, Colman, and Yeoman, J. Soc. Ch. Ind., 37, 319 T (1918)
11. Spielman and Wood, J. Soc. Ch. Ind., 38, 43 T (1919)
* See ref. 1, p. 4.

and then formed the pure alkali polysulfides by adding S to the mixtures. CS_2 was then passed into the mixtures. All operations were carried on in an atmosphere of hydrogen. The methods of analysis used by Yeoman and the possibility of his getting the results which he claims will be discussed in another part of this thesis.

The year 1925 found investigators especially interested in qualitative tests and in reactions of trithiocarbonates. Hirschkind[12] suggested the red to brown color produced by adding a few drops of 10% $Pb(OAc)_2$ solution to the sample as a test for a trithiocarbonate. Papineau, Couture, and Glosse[13] recorded many qualitative color tests, which together with those noted by Mang[14] will be recorded in another part of this thesis. Mang[15] also pointed to the presence of trithiocarbonates as the cause of the "dark viscose" which is encountered in the manufacture of artificial silk.

The author has attempted in this introduction to familiarize the reader with the nature of trithiocarbonates in general. It is his intention to limit the remainder of this thesis to a discussion of the preparation and properties of barium trithiocarbonate.

12. Hirschkind, W., Eng. Min. J. Press., 119,968-70 (1925)
13. Papineau, Couture, and Glosse, Ing. Chim., 9,176-8 (1925)
14. Mang, W., Rev. gen. mat. plastiques, 2, 357-61 (1926)
15. Mang, W., Kunstseide, 7,277-80 (1925)

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14. Hung, T., Rev. gen. mat. plastiques, 2, 557-61 (1926)
15. Hung, T., Kunstseide, 7,277-80 (1925)

Chapter I

A Consideration of Previous Methods of Preparing Barium Trithiocarbonate

The author intends in this chapter to consider the various methods of preparing barium trithiocarbonate which have been suggested in the literature. Some of the methods were developed for the preparation of trithiocarbonates other than barium trithiocarbonate, and the possibility of adapting them to the preparation of barium trithiocarbonate will be discussed. The author has attempted to give the credit in so far as is possible to the original author of each method. In instances in which a method has occurred several times in the literature the earliest dated reference has been given.

In 1886 Veley[16] prepared a yellow solid which he could not analyze, but which he believed was barium trithiocarbonate. The yellow solid was prepared by passing a stream of H_2 saturated with CS_2 through a freshly-prepared solution of $Ba(HS)_2$. The $Ba(HS)_2$ was prepared by passing H_2S into an aqueous solution of $Ba(OH)_2$. The CS_2 converted the $Ba(SH)_2$ to $BaCS_3$ according to the following equation: $Ba(SH)_2 + CS_2 \rightarrow BaCS_3 + H_2S$. The $BaCS_3$ was precipitated from the solution with alcohol and dried in a vacuum. Veley's inability to analyze his product was no doubt due to the fact that $BaCS_3$ decomposes in water slowly.

Yeoman,* some years later, repeated Veley's work, and claimed good results. Yeoman also claimed to have analyzed the

16. Veley, J. Chem. Soc. 49, T 369 (1886)
* See ref. 1, p. 4

substance using ordinary empirical methods. The author of this thesis also prepared barium trithiocarbonate by this method but was unable to prepare as pure a product as that claimed by Yeoman. It is the opinion of the author that the methods of analysis used by Yeoman were inaccurate. The reasons for making this statement will appear later in this thesis.

Yeoman* also suggested that $BaCS_3$ could be prepared by passing a stream of hydrogen saturated with carbon disulfide into barium hydroxide which was suspended in alcohol. This method was discarded by the author due to the small yield obtained.

Another method, somewhat similar to the above methods, is stated by Vanino.[17] A translation of Vanino's method follows: Saturate a solution of 16 grams of crystallized barium hydroxide, dissolved in 50 c.c. of warm water, in a closed flask with hydrogen sulfide. Mix the barium hydrosulfide solution with a warm solution containing an equal amount of barium hydroxide. Pour in the liquor 8 grams of carbon disulfide. This precipitates the barium trithiocarbonate as fine yellow crystals. Filter and wash with a little water, then with one-half strength alcohol, finally with pure alcohol. Dry on a steam bath. The addition of more alcohol precipitates more of the thiocarbonate. Yield, 12-15 grams.

The writer found this method to be rapid but discarded it due to the impurities found in the product. The chief impurity was barium hydroxide.

* See ref. 1, p. 4
17. Vanino, L., Praparative Chem. I Band, p. 381 (1921)

Vanino also suggested a method of preparing barium trithiocarbonate which was similar to the method used by Sestini* in 1883. Sestini prepared a mixture of the thiocarbonates of potassium and calcium by refluxing at 60° C. a mixture of 200 grams CS_2, 200 grams K_2CO_3, 200 grams CaO slaked with 100 grams H_2O, and 1000 grams H_2O, for ten hours. This product was used as a remedy against a vine disease known as phylloxera. The author's translation of Vanino's adaptation to barium trithiocarbonate follows; Place 50 grams $Ba(OH)_2$ in a round-bottomed 500 c.c. flask and cover the solid with 125 c.c. of CS_2. Close the flask with a cork stopper to which has been attached a reflux condenser, and heat gently for two hours. Control the temperature by a water bath. If the yellow residue appears dry, add 50 c.c. of CS_2. At the end of the reaction distill off the excess carbon disulfide. Yield, 95%. The author prepared $BaCS_3$ according to the directions, heating the mixture on a steam bath for two hours. The presence of white barium hydroxide could be detected in the yellow product. The product appeared to be crystals of barium hydroxide coated with a film of the yellow barium trithiocarbonate. Thinking that the two-hour refluxing period was too short a time to get a pure product the author repeated the procedure several times using refluxing periods of as high as ten hours. In each instance barium hydroxide could be detected under a microscope. The author concluded that the 95% yield mentioned by Vanino referred simply to the yield of the unpurified product. The results of the above experiments were

* See ref. 5, p.5

reported to Dr. L. C. Newell in a memorandum dated December 17. 1928. Dr. Newell suggested that an attempt be made to purify the product. An attempt to purify the product based on the difference in solubility of barium hydroxide and barium trithiocarbonate resulted in an unsatisfactory, but purer product. The method was abandoned, and the search for a better method was continued. The author has since concluded that complete purification probably could not have been obtained due to partial hydrolysis of the barium trithiocarbonate.

Another method of preparation depending on the reaction between carbon disulfide and barium hydroxide to get the barium trithiocarbonate is indicated in the following translation of Wilhelm Mang's* experiments on trithiocarbonates. A solution of barium hydroxide saturated at 50° C. is added to carbon disulfide. The mixture is left on a water bath at a temperature a little below the boiling point of carbon disulfide. The solution which is at first colorless later changes gradually from yellow to dark orange. On cooling, the barium hydroxide should not be precipitated. To obtain crystallization it is necessary to evaporate the solution on a water bath nearly to dryness. On cooling there is obtained a mass of fine crystals which appear to the eye to be perfectly homogeneous. Under a microscope the mass is seen to be composed of two distinct kinds of crystals. One part of the mass is composed of fine needle-like, colorless crystals of barium hydroxide while the other part is characterized by large yellow, double hexagonal, pyramid crystals which are presumably barium trithiocarbonate. Mang attempted to

* See ref. 14, p. 8

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Another method of preparation depending on the reaction between carbon disulfide and barium hydroxide to get the barium trithiocarbonate is indicated in the following translation of Wilhelm Lang's* experiments on trithiocarbonates. A solution of barium hydroxide saturated at 5° C. is added to carbon disulfide. The mixture is left on a water bath at a temperature a little below the boiling point of carbon disulfide. The solution which is at first colorless later changes gradually from yellow to dark orange. On cooling, the barium hydroxide should not be precipitated. To obtain crystallization it is necessary to evaporate the solution on a water bath nearly to dryness. On cooling there is obtained a mass of fine crystals which appear to the eye to be perfectly homogeneous. Under a microscope the mass is seen to be composed of two distinct kinds of crystals. One part of the mass is composed of fine needle-like, colorless crystals of barium hydroxide while the other part is characterized by large yellow, double hexagonal, pyramid crystals which are presumably barium trithiocarbonate. Being attracted to

* See ref. 14, p. 6

separate the crystals by adding alcohol to a concentrated solution of the two substances, thereby taking advantage of differences in solubility of barium hydroxide and barium trithiocarbonate in alcohol. The barium trithiocarbonate is only slightly soluble in alcohol while most of the barium hydroxide stays in solution. Mang noted the uniformity of his product under a microscope and made some qualitative tests, but did not attempt to analyze it quantitatively. Mang did not state how much of a yield he obtained. The author of this thesis prepared barium trithiocarbonate according to the method used by Mang but was unsatisfied with the yield obtained which was less than 10% of the theoretical yield, and continued his search for a satisfactory method of preparing barium trithiocarbonate.

Chapter II

Some of the Author's Experiments on Trithiocarbonates

In this chapter the author has included copies of some of the memorandums which he sent to Dr. Lyman C. Newell during the development of this thesis. Only preliminary investigations are recorded in this chapter.

December 17, 1928

To: Dr. Lyman C. Newell
From: C. P. Baker
Subject: Preparation of barium thiocarbonate

I prepared $BaCS_3$ according to the directions prepared from similar directions for the preparation of $CaCS_3$ mentioned in a British patent and carried out by G. Stamatoff. In my first attempt I heated on a steam bath with reflux condenser for two hours. The presence of white barium hydroxide could be detected in the yellow barium thiocarbonate product.

I repeated the above experiment, this time heating for six hours in addition to allowing the mixture to stand over night. The result was a uniform yellow product. Yield of unpurified product was 88%.

The next attempt was to prepare the barium thiocarbonate from directions given in Vanino's "Praparative Chemie",* similar to those given by Biltz. I found these directions satisfactory. The yield is not as large but probably contains less of the barium hydroxide as an impurity than the previous product.

The two methods of preparing the thiocarbonate go well together since the student can complete the procedure in Biltz while waiting for the reaction to take place on the steam bath in the British procedure.

* See ref. 17, p. 10

January 2, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: Barium Thiocarbonate

A brief search of the literature revealed nothing of value concerning barium thiocarbonate.

I attempted to purify barium thiocarbonate on the basis of solubility without results. All of the yellow salt went into solution and left a white mixture of barium hydroxide and a trace of barium carbonate. I concluded that the carbon disulfide-reflux method, although apparently giving a good yield, actually gives a very poor yield, as most of the product is barium hydroxide crystals covered with a thin layer of barium thiocarbonate.

The hydrogen sulfide method (Biltz) appears to give the purer product.

I attempted to neutralize the barium hydroxide with hydrochloric acid and decomposed the thiocarbonate as might have been expected. The reactions probably were:

$$BaCS_3 + 2HCl \rightarrow BaCl_2 + H_2CS_3$$

$$H_2CS_3 \rightarrow H_2S + CS_2$$

January 7, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: Barium Thiocarbonate

Since writing the last report (Jan. 2.) I found the following information in Chemical Abstracts vol. 20, no. 21, p. 3402, 1926. "Ba thiocarbonate was prepd. by adding CS_2 to a solu. of $Ba(OH)_2$ which was satd. at 50^o and heating on the water bath below the b. p. of CS_2 until no $Ba(OH)_2$ cryst. out on cooling. On evapg. almost to d ryness and cooling there seps. a mixt. of crystals of $Ba(OH)_2$ and (presumably) $BaCS_3$, as large yellow double-hexagonal pyramids. The latter are pptd. with alc. and are sol. in hot water to a dark orange solu., which gives the characteristic reactions of Na_2CS_3 solu. on addn. of $Pb(OAc)_2$, Fe_3Cl_6, and $CuSO_4$, but without interference of polysulfides. On heating $BaCS_3$ decomposes to BaO and S."

I took some of the barium hydroxide-thiocarbonate mixture, added an equal volume of water and brought it to a boil. Most of the thiocarbonate went into solution leaving a barium hydroxide sludge. I filtered off the clear liquor and precipitated out the thiocarbonate with alcohol. This gave a product which I think contains le ss barium hydroxide.

I added some $CuSO_4$ solution to a solution of $BaCS_3$ and obtained a heavy dark brown precipitate suggested as a test for a thiocarbonate. On heating the $BaCS_3$ decomposed leaving a white powder and giving off first CS_2 and then SO_2. The reactions probably were:

$$BaCS_3 \rightarrow BaS + CS_2$$

$$2BaS + 3O_2 \rightarrow 2BaO + 2SO_2$$

February 18, 1929.

To: Dr. L. C. Newell
From: C.P. Baker
Subject: Thiocarbonates

I attempted to determine the relative purity of two previously prepared yields of barium thiocarbonate; one prepared by the vacuum process and the other by precipitation with alcohol. The vacuum-process thiocarbonate was greenish-yellow and I suspected the presence of barium sulphide as it is yellow to green in color and might be formed by decomposition of the barium thiocarbonate. The addition of lead acetate, however, precipitated flocculent vermilion lead thiocarbonate without a noticeable trace of lead sulfide in the freshly precipitated stage. There did appear a trace of a milky precipitate which did not settle out as the vermilion precipitate which may have been lead hydroxide. This milky precipitate did not appear when lead acetate was added to the thiocarbonate precipitated by alcohol, instead, a clear liquid in which the vermilion precipitate formed resulted. The apparent insolubility and uniformity of the lead thiocarbonate caused me to attempt a quantitative analysis of the two samples of thiocarbonate.

The proposed method of analysis was to precipitate the thiocarbonate as lead thiocarbonate by adding lead acetate solution, let settle, decant, wash once with water the insoluble vermilion precipitate, add water and boil decomposing the lead thiocarbonate to lead sulfide, filter on a weighed filter paper, dry, weigh the sulfide precipitate, andcalculate

back to barium thiocarbonate.

I weighed out exactly a half gram of each sample and dissolved separately in cold water, nearly a liter of water was required for each sample as they went into solution very slowly since hot water could not be used without decomposing the thiocarbonate. The analyses were interrupted at this point. The next day I found the lead thiocarbonate completely decomposed into the fine-grained black lead sulfide. I continued the analysis but, probably due to failure to wash the precipitate, results of over 100% were obtained.

February 25, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: Thiocarbonates

I continued my study of the quantitative analysis of Barium Thiocarbonate by repeating the procedure outlined in the last report up to the lead sulfide point. Then, instead of drying and weighing the lead sulfide precipitate I converted the lead sulfide to lead sulphate, as suggested at our last meeting, filtered on quantitative filter paper, burned the paper, and weighed the lead sulfate residue. The results were unfavorable.

ANALYTICAL DATA

alc. ppt. $BaCS_3$		vac. process $BaCS_3$	
20.2110		20.2033	
19.7900		19.7900	
.4210	gr. sample	.4133	gr. sample
15.9158		16.6296	
13.5920		15.9520	
2.3238	gms. $PbSO_4$	1.1776	gr. $PbSO_4$

An analysis of the above results show them to be worthless. The abnormally large weight of lead sulfate may have been due to the occlusion of lead acetate used to precipitate the lead thiocarbonate. Time did not permit me to check this up.

March 3, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: Analysis of $BaCS_3$

I continued my study of the quantitative analysis of barium thiocarbonate. The following steps were carried out:

(1) Dissolved sample in 3N lead acetate solution:

Possibilites in the solution: $Ba(OH)_2$; any BaS not decomposing in the cold, Barium thiosulphate sample impurity, barium polysulphide, and the desired lead thiocarbonate vermilion precipitate.

(2) Boiled for about twenty minutes.

Result is formation of lead sulphide. Any barium sulphide would decompose.

(3) Filtered off lead sulphide precipitate.

(4) Washed with hot water until filtrate gave no further test for lead acetate.

A few white specks remained with lead sulphide in case of vacuum-prepared sample.

(5) Dissolved lead sulphide from filter with hot dilute hydrochloric acid.

(6) Added sulphuric acid to precipitate lead as sulphate.

(7) Let stand overnight to allow crystals to grow.

(8) Filtered on balanced filter paper.

(9) Dried at 51° C. until constant weight (about 1 hr.)

(10) Calculated back to barium thiocarbonate.

ANALYTICAL DATA

Alc. ppt. $BaCS_3$

$$\begin{array}{r} 10.8150 \\ \underline{10.5200} \\ .2950 \end{array} \text{ gm. sample}$$

Wt. of $PbSO_4$ (alc.)

1st weighing .3984
2nd " .3974
3d " .3974

Calculation to $BaCS_3$

$$.3974 \times \frac{\overset{BaCS_3}{245}}{\underset{PbSO_4}{303}} = .3213 \text{ gms. } BaCS_3$$

Percent. Purity

$$\frac{.3213}{.2950} \times 100 = 108.9\%$$

vac. process $BaCS_3$

$$\begin{array}{r} 10.7271 \\ \underline{10.5164} \\ .2107 \end{array} \text{ gm. sample}$$

Wt. of $PbSO_4$ (vac.)

1st. weighing .2671
2nd " .2620
3d " .2620

Calculation to $BaCS_3$

$$.2620 \times \frac{245}{303} = .2118$$

Percent Purity

$$\frac{.2118}{.2107} \times 100 = 100.5\%$$

I attempted to dissolve the lead sulphate in ammonium acetate in order to determine if any barium sulphate was present but the results were not quantitative.

March 11, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: A Method of Preparing $BaCS_3$

I tried out the new method of preparation suggested at our last conference making one major change. I omitted to displace the air with hydrogen for the following reasons:

1. By subjecting the mixture to high vacuum some of the CS_2 vaporizes and displaces the air dissolved in the mixture.
2. The vacuum draws out a higher percentage of air than could be displaced by hydrogen.
3. The process is made simpler.

The steps in the modified preparation are as follows:

1. Pulverize 20 grams of barium hydroxide. (The barium hydroxide used contained about .6% of Ca salts which may have caused the difficulty in the analytical procedure previously reported.)

2. Suspend the barium hydroxide in about 300 c.c. of alcohol in a 500 c.c. flask.

3. Add an excess of carbon disulfide (150 c.c.) as some is lost before reacting.

4. Connect the flask to a long vertical condenser and prepare for later heating with a water bath.

5. Connect the top of the condenser to the vacuum and start the vacuum pump. The water bath should be cool and no water should be in the condenser at this time.

6. After the air has been displaced, warm the water in the water bath and start the cold water flowing in the condenser jacket.

7. Adjust the vacuum and water-bath temperature so that the reflux action can take place at from 30 to 50° C. Allow to reflux for 3 or 4 hours.

8. Stop reflux action by draining water from condenser jacket. This allows the carbon disulphide to be driven off.

9. Concentrate the alcoholic mixture to about 150 c.c. using vacuum. This is not necessary if all the carbon disulphide has been driven off previously.

10. Filter and dry on a suction filter.

The above method gives a good yield (over 50%) and good quality product. The purity of the product I believe depends on the purity of the barium hydroxide used and time of refluxing. To my knowledge the use of the reflux on an alcoholic suspension has never been carried out or the idea of a vacuum reflux to remove the oxygen ever been made use of, in preparing thiocarbonates.

I attempted to reflux a saturated alcoholic solution of barium hydroxide without an excess of barium hydroxide. No yield was obtained.

The addition of a very dilute solution of copper sulfate to some of barium thiocarbonate gave a flesh-color flocculent precipitate. This precipitate which is probably copper thiocarbonate seems to be more stable than the lead thiocarbonate. On boiling the mixture black cupric sulphide was not formed as I expected, but an orange precipitate was formed

instead. Using more copper sulfate the black CuS was formed.

March 18, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: The Use of a Stirrer in Vacuum Reflux Method

I attached a stirrer to a 500 c.c. flask and made two four-hour runs following the directions outlined in the Vacuum Reflux Method of the March 11th report. The first run gave a fairly good-looking product, but of low yield; the second run gave a green-colored substance. I have concluded that stirring prevents proper refluxing from taking place and is not necessary.

I repeated my tests of $BaCS_3$ with a freshly-prepared 10% solution of $CuSO_4$, and got a black precipitate (CuS) on each attempt. I started two analyses but was unable to finish them.

April 1, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: Barium Thiocarbonate

I prepared barium thiocarbonate from the barium hydroxide containing less than .01% calcium salts. The vacuum reflux method was used. The product was separated from the alcohol on a suction filter and then placed in a test tube. No other means of drying was used.

I next attempted to analyze the product by converting to cupric sulfide, washing, dissolving in nitric acid and plating out the copper electrolytically. After several attempts continually getting a black, loose copper deposit, I analyzed the product by precipitating as lead thiocarbonate, washing, dissolving in hydrochloric acid precipitating as lead sulfate by adding sulfuric acid.

The analysis calculated on a dry basis gave 76.3% $BaCS_3$. A little of the barium sulfate passed through the filter paper, and the sample was not absolutely dry causing the results to be lower than they should have been.

April 8, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: Barium Thiocarbonate

In accordance with our conversation of last week I made a determination for dryness and found nearly 17% dampness, probably alcohol. This would have raised the calculated purity of last week's results to 93%. I repeated the analysis and attempted to shorten it by dissolving the lead thiocarbonate in H_2SO_4 omitting the HCl, but the results were not favorable.

I reviewed the different methods of analysis which I have made and reported to you in my various reports. The lead acetate methods described in the March 3 and April 1 reports seem the most promising.

I attempted to prepare $BaCS_3$ by refluxing BaS and CS_2. $BaCS_3$ was formed but was more impure than by other methods. The BaS was not as pure as might have been expected. The process might be developed by further study to give a better product.

April 15, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: Thiocarbonates

I made another attempt to prepare Barium Thiocarbonate by refluxing BaS with CS_2. This time I refluxed for eight hours without vacuum as my vacuum pump was out of order. The product before drying was green and turned to yellow on driving off the excess CS_2.

I next attempted to prepare some $MgCS_3$ by the Berzelius method suggested on page 19 of E. W. Yeoman's article of which you have a copy. $MgSO_4$ is added to $BaCS_3$ giving $MgCS_3$ and $BaSO_4$ which is filtered off. The yellow $MgCS_3$ solution was then partially evaporated under suction obtained from a water pump. The evaporation was slow and I was not able to complete my work. The possibilities, however, look promising. The $BaCS_3$ water solution is red while the $MgCS_3$ is citron yellow.

Below I have outlined several methods for preparing barium thiocarbonate.

1. Prepare barium hydrosulfide by passing hydrogen sulfide into a saturated solution of barium hydroxide. Add equal amounts of warm barium hydroxide solution and precipitate barium thiocarbonate with carbon disulfide. Wash with water and alcohol. Impure product resulted.

2. Reflux barium hydroxide with carbon disulfide for two hours. Result was barium hydroxide coated with barium thiocarbonate for both two and eight-hour runs.

3. Reflux barium hydroxide suspended in alcohol with excess of carbon disulfide under vacuum. (March 11). Result very good.

4. Same as No. 3 with stirring. Product not as good as in No. 3.

5. Refluxing barium sulfide with carbon disulfide. Product was not pure.

6. Same as No. 3 using barium sulfide instead of barium hydroxide. I have not tried this. Do you think it would work?

May 6, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: Magnesium Thiocarbonate

I attempted to prepare $MgCS_3$ by passing H_2S saturated with CS_2 into alcohol in which MgO was suspended, as suggested in Yeoman's article p. 19. The gas was passed in for about eight hours with only a small amount of the MgO converted to $MgCS_3$. As $MgCS_3$ is more insoluble in ether than alcohol I decided to suspend part of the partially converted mixture in ether and pass the gas through it for four hours more. This resulted in a more rapid conversion, a yellow salt presumably $MgCS_3$ being formed.

The preparation of $MgCS_3$ from $BaCS_3$ by precipitating out the barium as $BaSO_4$ on addition of $MgSO_4$ has not as yet materialized. $BaCS_3$ being only slightly soluble in water required a large volume of water to get it into solution. The addition of the $MgSO_4$ solution precipitated the $BaSO_4$ which was filtered off. I then attempted to concentrate the filtrate which should contain $MgCS_3$ by vacuum evaporation at room temperature. The rate of evaporation is very slow and in ten hours had not concentrated enough to throw any of the $MgCS_3$ out of solution. I did not heat the solution for fear of decomposing the $MgCS_3$. A small amount of the yellow solution on being heated in a test tube precipitated a white salt.

May 20, 1929.

To: Dr. L. C. Newell
From: C. P. Baker
Subject: Magnesium Thiocarbonate

The $MgCS_3$ which I prepared May 7 and placed in a stoppered test tube was found to have decomposed completely into a white powder. This indicates that the $MgCS_3$ is much less stable than the $BaCS_3$.

I prepared some more $MgCS_3$ by passing H_2S saturated with CS_2 into MgO suspended in ether. I then divided the yellow $MgCS_3$ formed into two portions. One portion I kept submerged in CS_2 and the other I put away in contact with CS_2 and H_2S vapors but not actually wetted by liquid CS_2. Observation of the products from time to time shows slight, if any, indication of decomposition.

I made another attempt to prepare $MgCS_3$ by metathesis from $BaCS_3$ and $MgSO_4$, but without good results. The $BaSO_4$ can be filtered off but the $MgCS_3$ left in the filtrate will not stand even vacuum evaporation without decomposing.

The $BaCS_3$ I prepared a month previous was found to have decomposed into a white powder.

Chapter III

A New Method of Preparing Barium Trithiocarbonate

The author wishes to call the attention of the reader to a few important facts concerning the preparation of trithiocarbonates which became evident as the experimental work proceeded. Experiment showed that the apparatus must be kept reasonably free from air to prevent the oxidation of the trithiocarbonate from taking place, that the temperature must not be allowed to rise above 50^{o} C. or decomposition will take place, that refluxing a mixture of barium hydroxide, water, and carbon disulfide would not give a good product because the reaction does not go to completion in water, and that barium trithiocarbonate is practically insoluble in ethyl alcohol.

It was the above facts which suggested to the author the method which he has chosen to develop and call the "Partial Vacuum-Reflux Method."

The method in the earlier stage of its development is outlined in a memorandum to Dr. L. C. Newell dated March 11, 1929.* The author has found the following somewhat revised procedure to give a high-purity barium trithiocarbonate:

Place in a round-bottom liter flask 25 grams of barium hydroxide which has been previously pulverized. Add about 300 c.c. of ethyl alcohol and about 200 c.c. of carbon disulfide to the flask. Place the flask in a water bath and connect a vertical water-cooled condenser. From the top of the condenser connect a rubber tube to the suction. An ordinary

* See page 23

water suction pump will suffice. Start the suction and put some warm water in the water bath. The mixture should soon start to reflux. Regulate the suction so that most of the carbon disulfide will condense in the water-cooled condenser, and drop back again into the mixture. A small gas flame or an electric hot plate can be used to keep the water in the water bath at about 40° C. The color of the mixture will turn from colorless to yellow in a few minutes. Six to eight hours are required to get a high percent conversion. The process can be stopped and more carbon disulfide added if it is necessary. When the refluxing period has been completed, pour the contents of the flask into a liter beaker, let the mixture settle, and decant the carbon disulfide and alcohol from the yellow solid at the bottom of the beaker. A separatory funnel may be used to advantage to separate the carbon disulfide from the yellow mixture. The barium trithiocarbonate is then separated from the barium carbonate formed during the reaction by dissolving the barium trithiocarbonate in warm water, which should not be over 30° C. Alcohol is then added to precipitate the barium trithiocarbonate from the water solution. Filter off the precipitate on a suction filter, and dry it in an oven at 50° C. An 80 to 90 percent yield of barium trithiocarbonate of about 90% purity should result. The product should be placed either in a tightly stoppered container or over carbon disulfide. If barium trithiocarbonate is left open to the air it will completely decompose in a few days into a white powder.

The author believes, notwithstanding the claim of Yeoman*

* See ref. 1, p. 4

whose work will be referred to again later, that a product of very much higher purity would not be possible by any method in which the barium trithiocarbonate is exposed to the air for a very long period.

There are two outstanding advantages which the above method has over other methods. First, the refluxing temperature is lowered, and air is excluded by the use of suction, and second, the percentage conversion of barium hydroxide to barium trithiocarbonate is increased by having the barium hydroxide suspended in alcohol in which barium trithiocarbonate is practically insoluble.

The reaction which takes place is probably:

$$3Ba(OH)_2 + 3CS_2 \rightarrow 2BaCS_3 + BaCO_3 + H_2O$$

Chapter IV

Some Difficulties wth Standard Methods of Analysis

Several investigators have prepared barium trithiocarbonate in various degrees of purity, but few have attempted to analyze it. Berzelius[18] pointed out that, owing to their instability, trithiocarbonates can be prepared only with great difficulty. Veley* claimed that barium trithiocarbonate existed as a yellow solid, but he was unable to analyze it. Most investigators have identified trithiocarbonates by qualitative tests only. Yeoman** claimed to have analyzed barium trithiocarbonate using ordinary empirical methods of analysis, and to have obtained good results. The exact methods used by Yeoman are not clearly stated in the reprint of a thesis written by him and appearing in the literature. Acting on the suggestion that barium trithiocarbonate might be analyzed by ordinary empirical methods the author spent many days in the laboratory attempting to make use of several common analytical methods in analyzing his product. Some of the difficulties which were encountered are recorded in this chapter.

The author attempted to determine the carbon content of his product by combustion in an electric furnace as suggested in several texts on quantitative analysis. The results were varied and always over 100%. This was due to oxides of sulfur being absorbed along with the carbon dioxide. The combustion

18. Berzelius, Am. Phys. Chem. 11, 6, 450 (1826)
* See ref. 1, p. 4
** See ref. 16, p. 9

method was abandoned as soon as it became obvious that any solvent that would pick up the acid carbonate radical would also pick up the oxides of sulfur. Other methods of determining carbon were sought, but none were found that could be applied to a compound containing such a high percent of sulfur as is present in barium trithiocarbonate.

The author next considered the well-known Carius tube method of determining total sulfur. According to this procedure the sulfur is oxidized with nitric acid at a high temperature and pressure to sulfur trioxide. The sulfur trioxide formed is dissolved in water and washed into a beaker, precipitated with barium chloride, and weighed as barium sulfate. This is one of the methods suggested by Yeoman, and would be all right for any trithiocarbonate except the one in which the author is interested, namely; barium trithiocarbonate. The method is useless in this instance since the barium already present in the sample, causes the formation of the insoluble barium sulfate which is difficult to get out of the tube. The barium sulfate would also occlude any impurities that were present in the original sample. Consequently, the Carius method was considered unsatisfactory.

The only other element in barium trithiocarbonate which could be determined empirically was barium which is usually determined as a sulfate. The author ran several straight barium determinations with apparently very good results. But it is obvious that these results have very little value as small traces of barium present in the sample as hydroxide or carbonate would be included in the total percent barium indicated by the analysis.

After this experience, the author concluded that, in spite of Yeoman's claims for empirical methods, he would search for other methods of analysis.

The author next started a new line of attack. It was known that barium trithiocarbonate decomposed on heating according to the following equation: $BaCS_3 \rightarrow BaS + CS_2$. With this in mind the author attempted to analyze his product by placing a small quantity of the sample in a crucible, and weighing both together. The contents were heated strongly for an hour or so with a Bunsen burner until the barium trithiocarbonate was completely decomposed. The difference in weight was considered carbon disulfide. The residue was then placed in an Erlenmeyer flask, and the sulfur present as barium sulfide was determined by adding hydrochloric acid, collecting the volatile hydrogen sulfide in lead acetate, oxidizing the lead sulfide formed with hydrogen peroxide, and weighing the sulfur as a sulfate. From this weight the sulfur present in the original sample as a sulfide was calculated. A small white precipitate which remained in the Erlenmeyer flask was separated from the hydrochloric acid mixture, and recorded as insoluble matter. Sulfuric acid was then added to the filtrate, and the barium determined as barium sulfate. The barium present as barium trithiocarbonate was calculated from the weight of the barium sulfate precipitate. The method looked good, and the author spent many hours attempting to get results, but met with failure after failure. Minor changes in the procedure were made but with no better results. The results were, in all instances, low, much lower than seemed reasonable. It occurred to the author that some of the barium

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sulfide might be oxidized by heating in the early stage of the analysis. To check this possibility of error, several determinations of sulfur as a sulfide were made without previously heatint the sample. These determinations did not give correct results for the sulfur present as a sulfide due to partial oxidation of carbon disulfide. No insoluble residue, however, remained in the Erlenmeyer flask as had been noticed previously. This seemed to indicate that oxidation had taken place during the heating of the sample. An attempt was made to oxidize the carbon disulfide quantitatively, but without results. Carbon disulfide can be oxidized only with difficulty. Consequently, the author was obliged to abandon the method and search further.

The possibility of determining the carbon disulfide by positive instead of negative methods was next considered. Falieres,* in 1844, suggested a simple method for determining carbon disulfide in potassium trithiocarbonate which was used at that time as an insecticide. The trithiocarbonate was decomposed by adding sulfurous acid. The carbon disulfide freed was distilled into benzene and the increase in volume determined; the available carbon disulfide in the original sample was calculated from this increase in volume. A similar method was suggested by Müntz in 1883. Carbon disulfide was distilled from a sample of the trithiocarbonate to which zinc sulfate had been added. The carbon disulfide was collected in a graduated cylinder and the increase in volume was noted, as in Falieres'

* See ref. 2, p. 4

method. Müntz claimed good results. The results probably were sufficiently accurate for the industrial need of his time. Such methods, however, are out of keeping with the accuracy required in the present instance. The author, by this time thoroughly dissatisfied with the prospects of the methods used by previous investigators, started to develop his own method of analysis.

Chapter V

The Development of a New Method of Analysis

Mermet* in 1876 called attention to the fact that the addition of a few drops of lead acetate solution to a solution containing a trithiocarbonate produced a vermilion precipitate of lead trithiocarbonate. Mermet's results suggested to the author the possibility of analyzing barium trithiocarbonate by dissolving the sample in water, precipitating the trithiocarbonate radical as lead trithiocarbonate, converting to lead sulfate, and calculating the percent purity from the weight of the lead sulfate. Some of the earlier attempts to use this method met with the failures which were recorded in memorandums dated February 18, 25, and March 3, 1929.**

Several factors collectively caused the failures, but these factors were not known to the author at the time. Later experiments showed that too much of an excess of lead acetate had been used, that the excess lead acetate had not been completely washed out of the lead trithiocarbonate precipitate, that some of the barium trithiocarbonate had hydrolized before reacting, and that the dissolving of the lead sulfate from the filter paper, and the drying of the precipitate on a filter paper had introduced errors.

Since the experiments referred to above were completed changes have been made in the procedure used to correct the difficulties met. The new procedure which has emerged from the failures referred to follows: Weigh out about .2 grams of the

* See ref. 3, page 5
** See Chapter II

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* See ref. 3, page 5
** See Chapter II

sample, and place it in a liter beaker containing about 500 c.c. of lead acetate solution with .15 grams of lead acetate for every .1 gram of sample. Do not let the sample come in contact with pure water before it is added to the lead acetate solution or it will hydrolyze. Warm the solution to about 30° C. and agitate until the yellow barium trithiocarbonate is entirely converted to the insoluble red lead trithiocarbonate. Allow the mixture to stand until the solution above the red lead trithiocarbonate is clear, decant or syphon off the clear liquor, and test the liquor for lead with hydrogen sulfide. A test for lead indicates excess lead acetate. Wash until no excess lead acetate remains. Boil the mixture vigorously for about one-half hour to decompose the lead trithiocarbonate, and expel the resulting disulfide from the mixture. Wash once more with water. Add an excess of hydrogen peroxide, about 10 c.c. of a three percent solution, to the mixture, and boil until all of the lead sulfide is oxidized to lead sulfate. Filter the lead sulfate on a quantitative filter paper, and ignite in a weighed crucilbe. Some of the lead sulfate will be reduced to lead by the burning paper. Redissolve the lead by adding a few drops of nitric acid (dilute), and evaporate almost to dryness, add water and a few drops of sulfuric acid (dilute) to convert the lead nitrate to lead sulfate. Evaporate to dryness, and drive off the excess sulfuric acid by heating strongly on an electric heater. Use a crucible cover to prevent loss from spattering. Cool in a desiccator, and weigh. Calculate the percent barium trithiocarbonate in the original sample from the weight of the lead

sample, and place it in a liter beaker containing about 500 c.c. of lead acetate solution with .15 grams of lead acetate for every .1 gram of sample. Do not let the sample come in contact with pure water before it is added to the lead acetate solution or it will hydrolyze. Warm the solution to about 50° C. and agitate until the yellow barium trithiocarbonate is entirely converted to the insoluble red lead trithiocarbonate. Allow the mixture to stand until the solution above the red lead trithiocarbonate is clear, decant or syphon off the clear liquor, and test the liquor for lead with hydrogen sulfide. A test for lead indicates excess lead acetate. Wash until no excess lead acetate remains. Boil the mixture vigorously for about one-half hour to decompose the lead trithiocarbonate, and expel the resulting disulfide from the mixture. Wash once more with water. Add an excess of hydrogen peroxide, about 10 c.c. of a three percent solution, to the mixture, and boil until all of the lead sulfide is oxidized to lead sulfate. Filter the lead sulfate on a quantitative filter paper, and ignite in a weighed crucible. Some of the lead sulfate will be reduced to lead by the burning paper. Redissolve the lead by adding a few drops of nitric acid (dilute), and evaporate almost to dryness, add water and a few drops of sulfuric acid (dilute) to convert the lead nitrate to lead sulfate. Evaporate to dryness, and drive off the excess sulfuric acid by heating strongly on an electric heater. Use a crucible cover to prevent loss from spattering. Cool in a desiccator, and weigh. Calculate the percent barium trithiocarbonate in the original sample from the weight of the lead

sulfate in the crucible. The analysis requires about five hours, but gives good results considering the nature of the substance analyzed.

The following reactions take place:

$$BaCS_3 + Pb(OAc)_2 \rightarrow PbCS_3 + Ba(OAc)_2$$

$$PbCS_3 \rightarrow PbS + CS_2$$

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

Some of the analytical results obtained using the above procedure follow:

Analysis I

Wt. of weighing bottle and contents	12.0191
Wt. after removing sample	11.7333
Wt. of sample	.2858
Wt. of crucible and $PbSO_4$	13.7389
Wt. of crucible	13.4183
Wt. of $PbSO_4$	.3207

$.3225 \times \frac{245}{303} \times \frac{100}{.2858} = 91.3\%$ $BaCS_3$ in sample

Analysis II

Wt. of weighing bottle and contents	12.1586
Wt. after removing sample	11.7213
Wt. of sample	.4373
Wt. of crucible and $PbSO_4$	14.2857
Wt. of crucible	13.8137
Wt. of $PbSO_4$	.4720

$.4720 \times \frac{245}{303} \times \frac{100}{.4373} = 87.5\%$ $BaCS_3$ in sample (a little loss was caused by spattering)

Analysis III

Wt. of weighing bottle and contents	13.3830
Wt. after removing sample	12.9179
Wt. of sample	.4651
Wt. of crucible and $PbSO_4$	14.7920
Wt. of crucible	14.2756
Wt. of $PbSO_4$	.5164

$$.5164 \times \frac{245}{303} \times \frac{100}{.4651} = 89.9\% \text{ } BaCS_3 \text{ in sample}$$

Barium trithiocarbonate decomposes slowly when exposed to the air. This fact makes it improbable that a barium trithiocarbonate of 100% purity could be prepared and kept in pure form for a very long period.

Chapter VI
Some Physical and Chemical Properties of Barium Trithiocarbonate

Barium trithiocarbonate is a yellow solid at ordinary temperatures, and dissolves in water to form a reddish-colored solution. The exact solubility, however, is difficult to determine as barium trithiocarbonate hydrolyzes in water even at room temperatures. This is as one would expect since all salts formed from weak acids and strong bases hydrolyze. If hot water is used the trithiocarbonate will decompose immediately. The equation for the reaction taking place is probably:

$$BaCS_3 + 2H_2O + 2O_2 \rightarrow BaS_2O_3 + BaCO_3 + CS_2 + 2H_2S$$

The salt will decompose in a few hours if it is exposed to strong sunlight. If the barium trithiocarbonate is left in an open dish it will decompose completely in a few days, the exact time depends on the temperature and humidity of the surroundings. The author found that if kept in a tightly-stoppered test tube, the stoppered end of which had been dipped in paraffine, the trithiocarbonate salt kept for three or four months before showing indications of serious decomposition. The reactions which take place during decomposition in air appear to be:

$$BaCS_3 \rightarrow BaS + CS_2$$

$$BaS + H_2O \rightarrow Ba(OH)_2 + H_2S$$

$$Ba(OH)_2 + CO_2 \text{ (from air)} \rightarrow BaCO_3$$

The white residue resulting from decomposition is composed largely of $Ba(OH)_2$ and $BaCO_3$ with traces of BaS_2O_3.

The author observed that carbon disulfide was one of the

first products resulting from decomposition in air. This suggested the possibility of preventing, or at least minimizing, the decomposition by keeping the barium trithiocarbonate in an atmosphere of carbon disulfide. At the present writing, January 1930, the author has some barium trithiocarbonate which he prepared in March 1929, and has kept surrounded with an atmosphere of carbon disulfide. The trithiocarbonate does not appear to have decomposed.

An attempt was made to determine the effect of temperature on the rate of decomposition of the dry salt. A weighed amount of the trithiocarbonate was placed in a crucible and heated in a sand bath. The changes in weight are recorded in the accompanying table.

Decomposition Data

Wt. of sample at start	.5196
Wt. of crucible at start	15.6087
Wt. of crucible and sample at start	16.1283

Time	Temp. °C	Weight	Loss
1:45 P.M.	70	16.1283	0.0000
2:20	70	16.1053	-.0230
3:00	70	16.1065	+.0012
3:40	85	16.1034	-.0031
4:05	100	16.1028	-.0006
4:17	120	16.1020	-.0008
4:32	140	16.1006	-.0014
4:50	150	16.1009	-.0003
(left over night)			
10:00 A.M.	170	16.1018	+.0009
11:45	180	16.1012	-.0006
1:20 P.M.	190	16.1009	-.0003
2:30	195	16.0989	-.0020
3:50	200	16.0976	-.0013
4:45	210	16.0946	-.0030

Several other similar decomposition tests were made. Samples which were heated to temperatures above 260° C. ignited and burned with a rose-colored flame.

The following conclusions might be drawn from the above data:

1. The sample contained a little carbon disulfide or other volatile impurity which was driven off at the start.

2. The decomposition of dry barium trithiocarbonate does not increase rapidly with the temperature.

3. Dry barium trithiocarbonate is fairly stable.

4. Some oxidation was taking place during the heating. This is made evident especially by the gain in weight which took place over night.

5. The loss in weight is not the true decomposition loss since an increase in weight by oxidation was taking place simultaneously.

6. The sample took fire when the kindling temperature of carbon disulfide was exceeded. The samples did not all take fire at the same temperature due to variations in the rate of heating and amount of air in contact with the sample.

No treatment of trithiocarbonates would be complete without including something concerning the reactions of the trithiocarbonates with metallic salts. It was, no doubt, the many-colored trithiocarbonate salts which first aroused the curiosity of investigators. As far back as 1876 Mermet* proposed the addition of a nickel salt as a test. He claimed

* See ref. 3, page 5.

that one drop of a decinormal solution of a nickel salt, which has been decolorized by adding ammonium hydroxide, will detect one part of trithiocarbonate in sixty thousand parts of solution. A cherry-red tint is produced.

Hirschkind** suggests the following test for the detection of thiocarbonates in xanthates. To 50 c.c. of a solution to be tested for thiocarbonates add a little of a 10% solution of $Pb(OAc)_2$. If the solution turns red or brown the presence of thiocarbonates is indicated.

Several investigators, among whom are Papineau, Couture, Glosse#, and Mang,* studied the characteristic reactions which take place between trithiocarbonates and metallic salts. Some of the most frequently mentioned are given below.

Pb salts

An alkaline solution of a lead salt gives a red precipitate which is insoluble in an excess of the reagent, in a neutral or very slightly alcoholic solution, and gradually turns black on heating. The author of this thesis found the precipitate to decompose if allowed to stand or if warmed. The products of decomposition were lead sulfide, and carbon disulfide.

Ni salts

An alkaline solution of a nickel salt (containing tartaric acid) gives a splendid garned-red solution in the cold; in an ammoniacal solution the addition of a small amount of the reagent produces a wine-colored precipitate, which dissolves to give a garnet-red on addition of an excess of the reagent.

** See ref. 12, p. 8
# See ref. 13, p. 8
* See ref. 14, p. 8

Cd salts

The addition of cadmiun acetate to a trithiocarbonate solution gives a yellow precipitate which dissolves in an excess of the reagent to give a very deep yellow color.

Hg salts

The addition of a neutral solution of mercuric chloride in ammonium hydroxide produces a deep orange precipitate which gradually changes to a milk-chocolate brown. A fine black powder is formed if an excess of the reagent is added.

Fe^{++} salts

Alkaline solutions of iron salts (in the presence of tartrates) produce a wine-colored precipitate which turns black on adding more of the reagent, but has a deep wine-color tinge by transmitted light.

Fe^{+++} salts

Ferric salts give similar results, but are somewhat darker red by transmitted light.

Ag salts

The addition of silver nitrate gives a gelatinous flocculent precipitate which looks black, but is brownish-red by transmitted light, and is insoluble in excess of the reagent.

Cu salts

Copper salts produce a precipitate very similar to that produced by silver salts, but are extremely soluble in an excess of the reagent to give a brownish-red solution which turns lighter red if a large excess of the reagent is added.

Bi salts

The addition of an ammoniacal solution of a bismuth salt

to a solution of trithiocarbonate gives a dark brown precipitate.

Mang* listed the colors of the precipitates formed by adding salts of heavy metals to solutions of trithiocarbonates as follows:

Reagent added	Color of precipitate
$Pb(OAc)_2$	Cinnabar-red
Fe_2Cl_6	Brown
$AgNO_3$	Chocolate
$CuSO_4$	Dark brown
$SnCl_4$	Brown
$BaCl_2$	Yellow

Generally speaking, the colors first produced are the colors of the metal trithiocarbonates, but, as most of the trithiocarbonate salts are unstable, they hydrolyze on standing, forming either sulfides or oxides. The secondary color is the color of the resulting mixture. Qualitative color tests can be quickly made, and are used by most investigators to detect the presence of trithiocarbonate salts.

* See ref. 14, page 8

Conclusion

In the execution of this thesis the author has satisfied himself that a sulfur analogue of barium carbonate exists, and can be prepared in a relatively pure condition. Research has revealed several methods of preparing barium trithiocarbonate. The method which seems most promising, and which the author has been interested in developing is the so-called "Partial Vacuum-Reflux Method." In this method barium hydroxide is suspended in a mixture of alcohol, and carbon disulfide, and refluxed for several hours.

The problem of analyzing barium trithiocarbonate was found to be extremely difficult. This is due to the unusual occurrence of the elements barium, carbon, and sulfur, combined in the same compound. The presence of barium was found to interfere with most methods of determining sulfur, and the high percentage of sulfur present interfered with the analysis of carbon by combustion methods. A method was developed by the author which involves the conversion of the barium trithiocarbonate to lead trithiocarbonate with subsequent decomposition forming lead sulfide, which was followed by oxidation to lead sulfate. The percentage purity of the barium trithiocarbonate was calculated for the weight of the lead sulfate. This procedure requires a high degree of skill in analytical manipulation, but gives reasonable results.

Barium trithiocarbonate was found to be much less stable than barium carbonate. It decomposes slowly on exposure to air, and hydrolyzes almost instantaneously when hot water is added

to it. It was found that the substance could be preserved for long periods in an atmosphere of carbon disulfide.

The presence of the trithiocarbonate radical in solution can be detected qualitatively by adding any one of several solutions of heavy metal salts. In each instance a flocculent precipitate of a metal trithiocarbonate is produced which has a characteristic color. One of the most insoluble heavy metal trithiocarbonates is that of lead. The addition of lead acetate to a solution containing the trithiocarbonate radical will produce a flocculent vermilion precipitate which will turn black on heating. This has been found to be a very delicate test for trithiocarbonate.

In conclusion, the author suggests to any investigator who desires to add to present knowledge concerning trithiocarbonates that he attempt to prepare a pure magnesium trithiocarbonate, and analyze it. The reflux method does not give a good yield of the magnesium salt.

Abbreviations

J. Chem. Soc.	Journal of the Chemical Society (London)
Ann. Chim. Phys.	Annales de chimie de physique
Bull. Soc. Chem.	Bulletin de la societe chemique de France
Compt. rend.	Comptes rendus hebdomadaires des seances de l'academie des sciences
Gazzetta chim. ital.	Gazzetta chemica italiana
J. Soc. Ch. Ind.	Journal of the Society of Chemical Industry (London)
Eng. Min. J. Press.	Engineering and Mining Journal Press
Ing. chim.	Ingenieur chemiste
Rev. gen. mat. plastiques	Revue generale des matieres plastiques

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